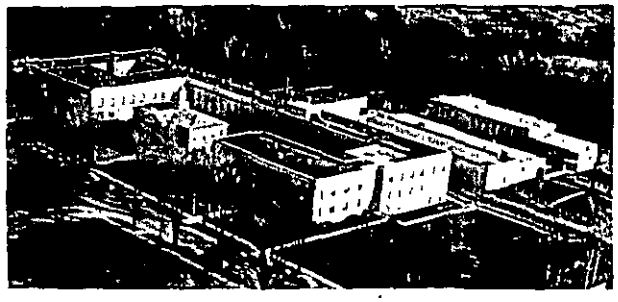

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

Project 2251

Report Two

to

PIONEERING RESEARCH COMMITTEE

August 21, 1961

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

THE MOLECULAR PROPERTIES OF HEMICELLULOSES

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A Quarterly Report

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THE MOLECULAR PROPERTIES OF HEMICELLULOSES

As a part of the study of hemicellulose polymers of varying complexity in their natural state and as derivatives, an opportunity has arisen to study the xylan polymers of black spruce (Picea nigra). They were obtained from pulps (1) which resulted from a series of digestions over a wide pH range.

At pH 9-11 of a typical sulfite cook the 4-O-methylglucuronoaraboxylan is intact. This parent polymer however, loses the glucuronic acid residue at the high pH of the kraft cook to become the araboxylan while, on the other hand, when wood digestion is done at low pH the arabinose sugar residue is removed and a glucuronoxylan is produced.

Removal of a sugar residue in this way from the parent polymer can be expected to result in a new macromolecule with different properties. This might be expected particularly when the charged glucuronic acid is removed. The extent of weight loss which occurs in the removal can also provide a clue to the degree of branching present which in turn affects the solubility and sorption characteristics of the polymer.

Two methods are commonly used to obtain polymer dimensions in solution. One of these is to determine the dependence of light scattering on scattering angle. This can be done only if the solution can be made rigorously free of aggregates or dust. This has not proven possible with the three natural polymers mentioned above although strenuous efforts were made to achieve adequate clarification. The expectation that little aggregation and easier clarification will be possible by using derivatives of the hemicelluloses are important reasons for their preparation and measurement.

The other method which can be used to obtain polymer dimensions is to use the viscosity-molecular weight relation of Flory (2). While this method is not ideally applicable unless the measurements are made on a monomolecular fraction in a neutral solvent, it provides a means of comparison between the polymers. The extent to which nonideal circumstances affect the dimensional data can be checked later on derivatives of the polymer, for example the acetate, in an organic solvent.

The intrinsic viscosity and molecular weight of the natural polymers from black spruce are listed in Table I. The measurements were made in a 2:1 molal ratio, sodium hydroxide:boric acid, in water. The slopes of the viscosity and light-scattering plots of most of the hemicelluloses show that this solvent is actually fairly neutral, i.e., the concentration dependence of the two measurements is small. The root-mean-square length dimension calculated from the Flory relation and its ratio to the theoretical fully extended length of the molecule, as well as the calculated constants which relate intrinsic viscosity to degree of polymerization of the polymers, are also listed in Table I.

Light-scattering analyses of the uronic acid-free araboxylan are not reported in Table I. Two attempts were made to make measurements on this polymer. On the first occasion it was found that residual color in the sample absorbed too much light to make light-scattering measurements possible. After the sample was purified further and measured again, aggregation occurred which gave falsely high molecular weights even though strongly alkaline sodium borate was used as the solvent. Overcoming aggregation (or crystallization) effects will be a matter of continual concern and study until a solution to the difficulty is found.

TABLE I

INTRINSIC VISCOSITY, MOLECULAR WEIGHT, AND LIGHT-SCATTERING DATA FOR SOME HEMICELLULOSES AND CELLULOSE DERIVATIVES

Sample	Pulp Type	pH of Cook	Intrinsic[c] Viscosity, dl./g.	Molecular[c] Weight $\bar{M}_w$	Degree of Polymerization, D.P.	Depolarization Factor, $f(\rho)$	Refractive Index Increment, dn/dc	Root Mean[a] Square End to End Length of Molecule, $(\bar{r}^2)^{1/2}$ cm. x 10^8	Maximum[b] End to End Length of Molecule, $\bar{r}_{max}$	Ratio $(\bar{r}^2)^{3/2}/\bar{r}_{max}$	Viscosity-[d] D.P. Constant, $K_{D.P.}$
Glucuronoaraboxylan	Sulfite	9-11	0.65	47,000	356	None	0.116	247	1780	0.138	548
Araboxylan	Kraft	ca. 13	0.61								
Glucuronoxylan	Acid sulfite	1-2	0.19	40,000	310	0.88	0.145	156	1590	0.097	1631
Slash pine hemicellulose			0.55	67,000	440	0.88	0.129	264	2266	0.116	800
Black spruce hemicellulose			0.52	42,000	288		0.171	221	1483	0.150	592
Galactoglucomannan, southern pine			0.27	27,600	181	0.813	0.180	155	930	0.167	670
Cellulose nitrate L-8 (4)			2.02	91.000	306		0.102	575	1530	0.350	152
Cellulose nitrate H-2 (4)			7.00	373,000	1257		0.102	1200	6270	0.180	179
Cellulose triacetate (2)			0.49	30.600	105			241	525	0.200	214

[a] The length was calculated from the Flory (2) relation $[\eta] = \Phi (\bar{r}^2)^{3/2}/M$ where $\Phi = 2 \times 10^{21}$ and M and $[\eta]$ are shown in the table.

[b] $\bar{r}_{max}$ is the length of the chain if the monomer units (5.15×10^{-8} cm. long) were stretched end to end.

[c] Both viscosity and light-scattering molecular weight determinations were done in a 2:1 molal ratio of NaOH:boric acid.

[d] In the relation D.P. = $K_{DP} \cdot [\eta]$.

Marked differences are shown between the parent glucuronoaraboxylan and the arabinose-free glucuronoxylan in Table I. The intrinsic viscosity and molecular weight and the mean end-to-end length calculated from them show that the glucuronoxylan is apparently much more tightly branched or coiled than the parent polymer. Although no molecular weight was obtained on the araboxylan, it, on the other hand, has lost little in viscosity although its molecular weight must be lower since the glucuronic acid residues were removed. This indicates that these residues are side groups not involved in the main chain of the polymer. Data on hemicellulose extracts from slash pine and black spruce as well as a galactoglucomannan from southern pine obtained in earlier research (3) have been included in Table I for comparison. The extract from slash pine consisted predominantly of glucuronoaraboxylan with smaller amounts of galactoglucomannan, while the extract from black spruce was predominantly a galactoglucomannan with a lesser quantity of glucuronoaraboxylan. It is seen in Table I that the ratio of mean length to maximum length is higher for both galactoglucomannan from southern pine and for the galactoglucomannan-rich extract from black spruce than for the xylan polymers; the latter are thus apparently more highly branched.

In general, the hemicelluloses are apparently either more branched or more tightly coiled than are the nitrate and acetate cellulose derivatives also listed in Table I for comparison. This is reflected by the increase in the K_{dp} constants (see footnote d to Table I) which show the unreality of using K_{dp} constant obtained on cellulose for the hemicelluloses and also the apparent unreality of using a like viscosity constant for all hemicelluloses. The threefold increase in the K_{dp} constant for glucuronoxylan over that of the parent polymer needs checking and confirmation by light-scattering measurements on these samples after acetylation.

Work is now being started on the acetates of 4-O-methylglucuronoaraboxylan, gum arabic, and cherry gum. Their preparation, reduction and study by viscosity and light-scattering photometry will be described in a following report.

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Norman S. Thompson, Research Associate

Harold A. Swenson, Research Associate
Cellulose Group